Arsenic Speciation

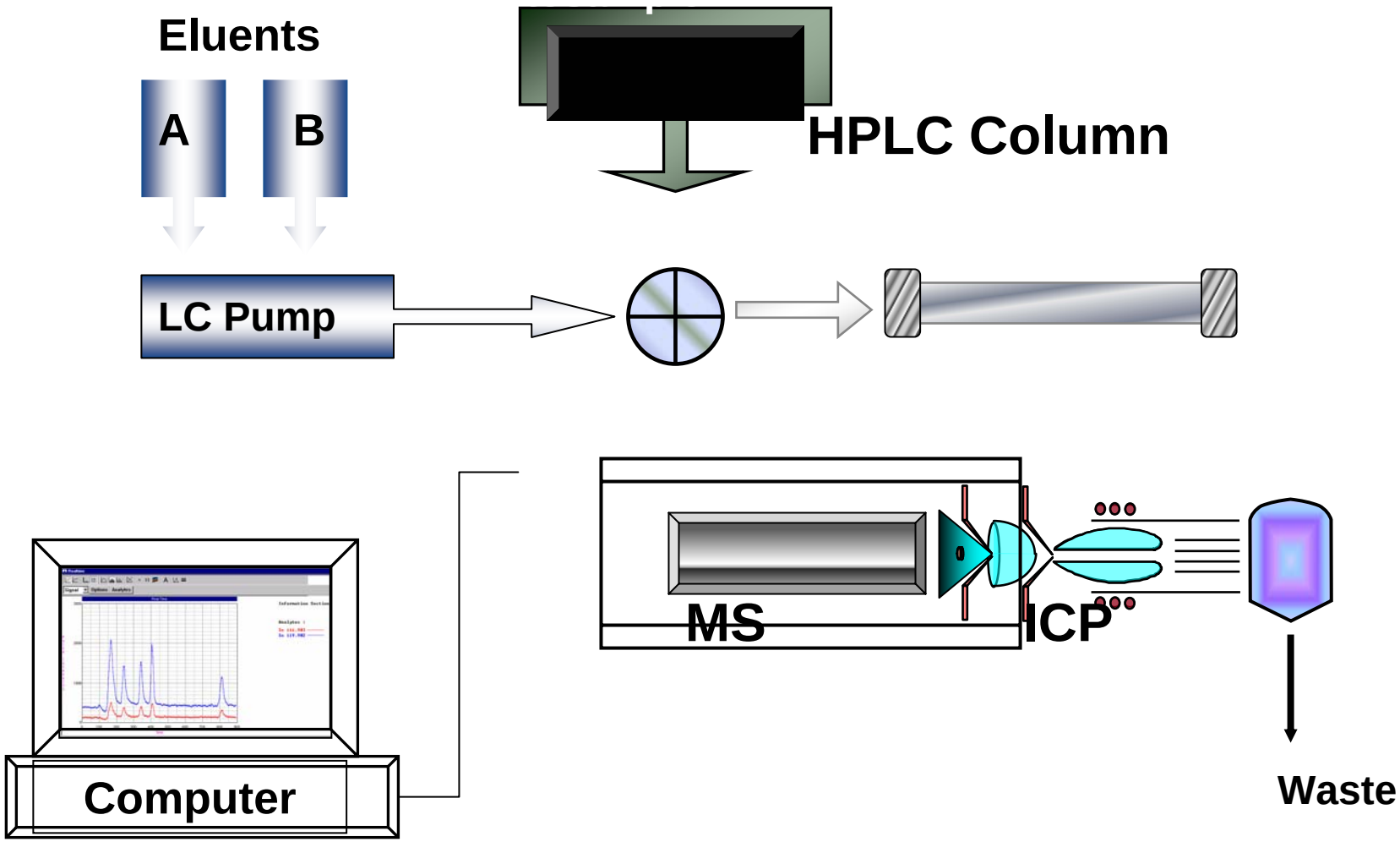
- Methods for analysis of MMA^{III} and DMA^{III}
- Problems of instability
- Uncharacterized arsenic species
- Binding of trivalent arsenic metabolites (e.g., with Hb) and arsenic in blood

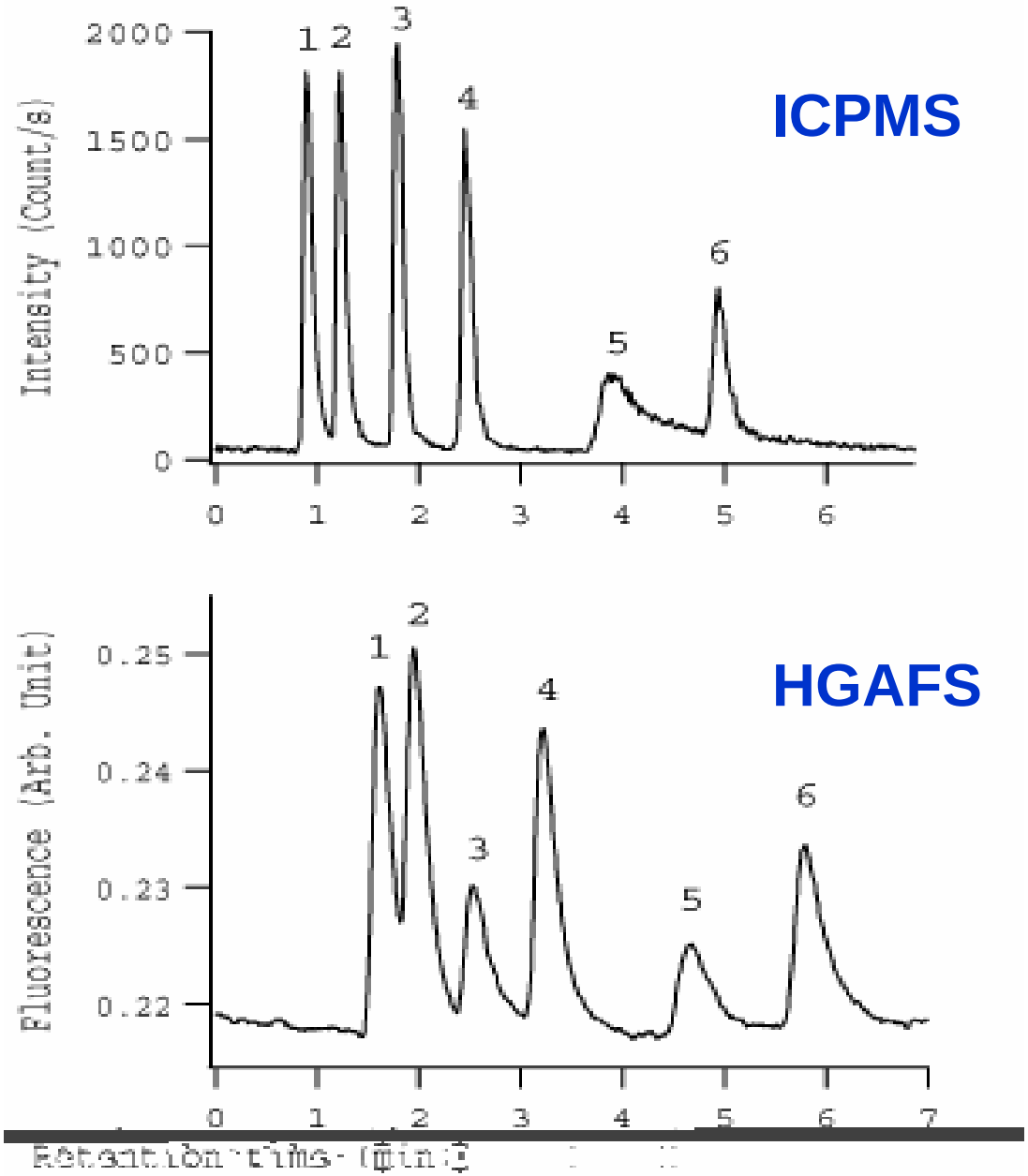
X. Chris Le

University of Alberta

Edmonton, Alberta, Canada

HPLC-ICPMS

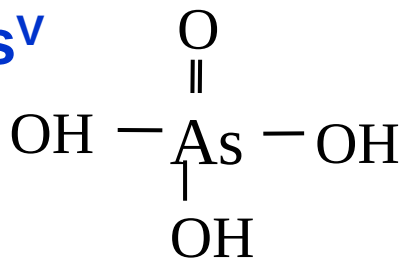




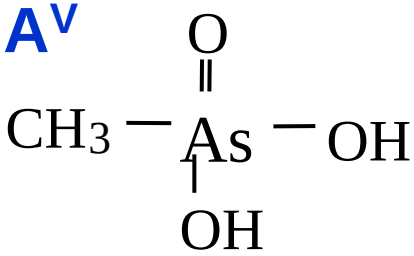
1, iAs^{III}
2, MMA^{III}
3, DMA^{V}
4, MMA^{V}
5, DMA^{III}
6, iAs^{V}

Hydride Generation

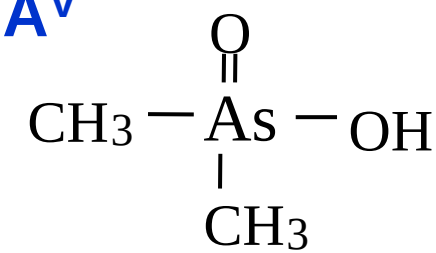
iAs^{V}



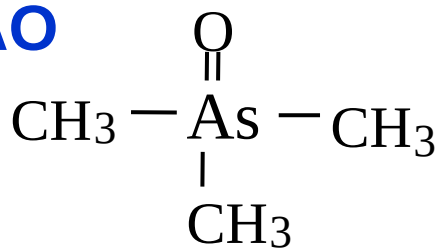
MMA^{V}



DMA^{V}



TMAO

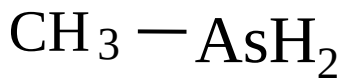


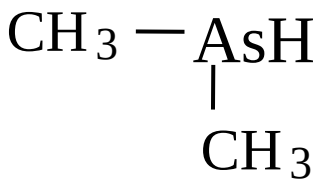
BH_4^-

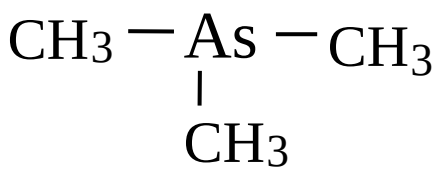
H^+

pH 1

Volatile arsines

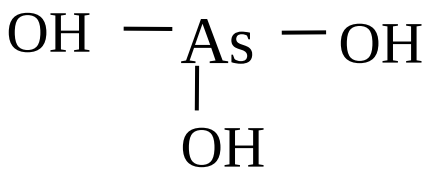




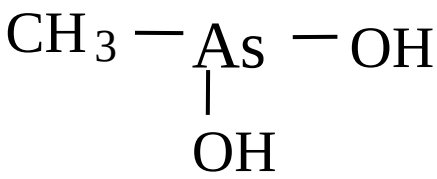


Hydride Generation

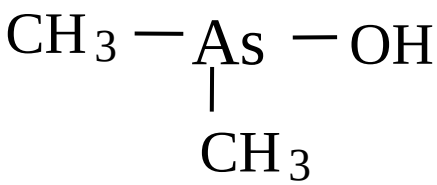
iAs^{III}



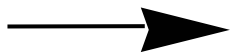
MMA^{III}



DMA^{III}



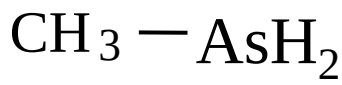
BH_4^-

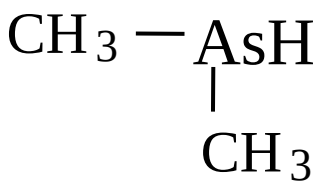


H^+

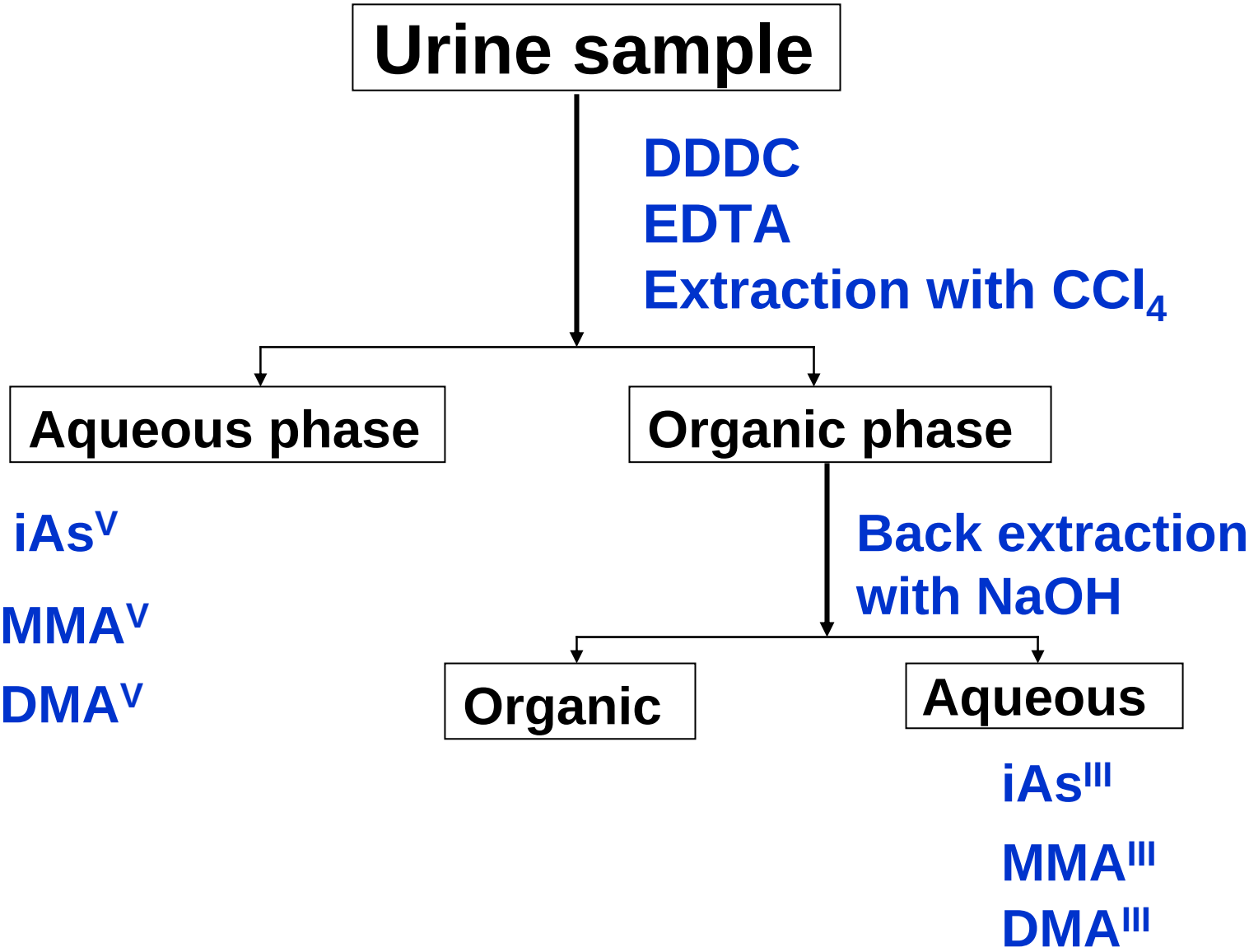
pH 6

Volatile arsines





Solvent Extraction

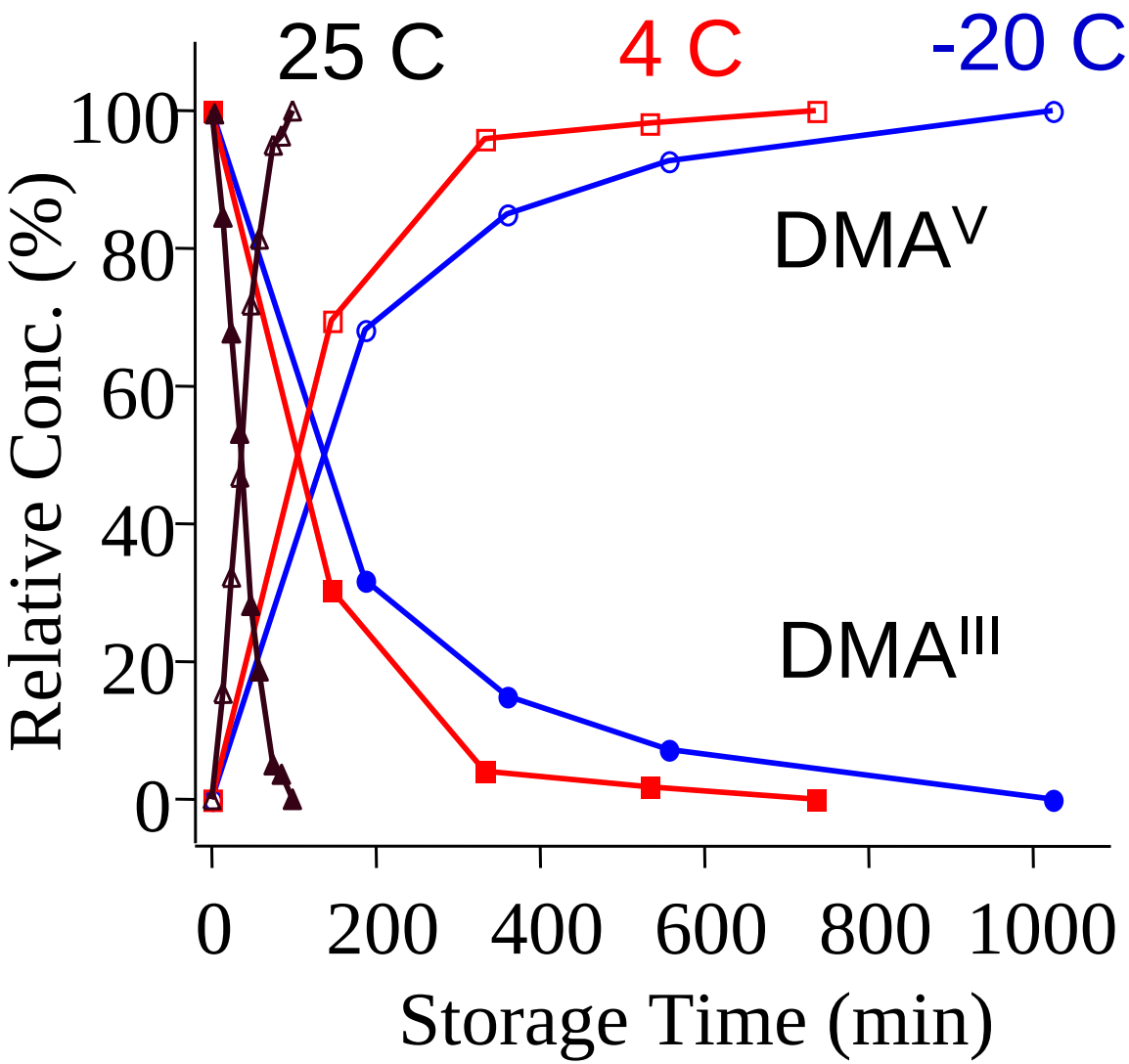


Methods of arsenic speciation analysis

1. **Direct HPLC separation with ICPMS or HGAFS detection**
   - Least alteration to the sample
   - Ability to analyze new arsenic species
2. **Selective hydride generation and GC-AAS**
3. **Selective solvent extraction followed by HPLC-ICPMS**
4. **Other methods based on chromatography and mass spectrometry**

2. Chang
spiked u

Change of DMA^{III} to DMA^{V} in urine



Valenzuela et al. *Environ. Health Perspect.* 113, 250-254 (2005).

- Morning urine samples
- Immediately frozen on dry ice
- Analyzed within 6 h after collection
- Hydride generation GC-AAS method
- The highest %DMA^{III} in urine ever reported

- DMA^{III} 49% DMA^{V} 23.7% Sum 72.7%
- MMA^{III} 7.4% MMA^{V} 2.8% Sum 10.2%
- iAs^{III} 8.5% iAs^{V} 8.6% Sum 17.1%

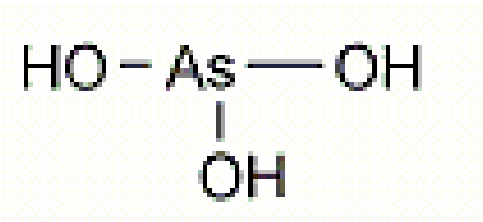
Reasons for the very high concentrations of DMA^{III} in human urine of this Mexico population

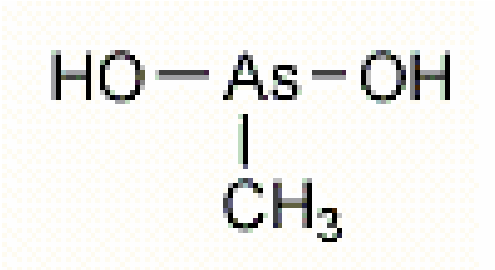
- **Minimal oxidation of DMA^{III} to DMA^{V}?**
- **Stability of DMA^{III} in these urine samples?**
- **Anything else special about this study population (e.g., diet)?**

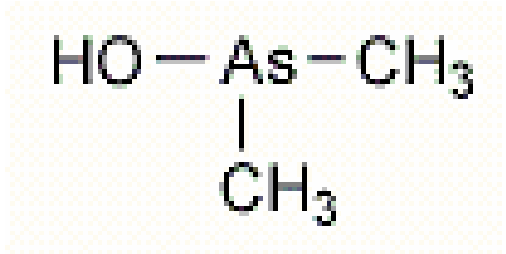
3. Arsenic species in blood and biological tissues

- **Urinary arsenic is a good marker of exposure**
- **Arsenic speciation in other biological samples is useful for studying metabolism and toxicity**
- **Protein interaction with trivalent arsenic metabolites**

iAs^{III} **MMA^{III}** **DMA^{III}**



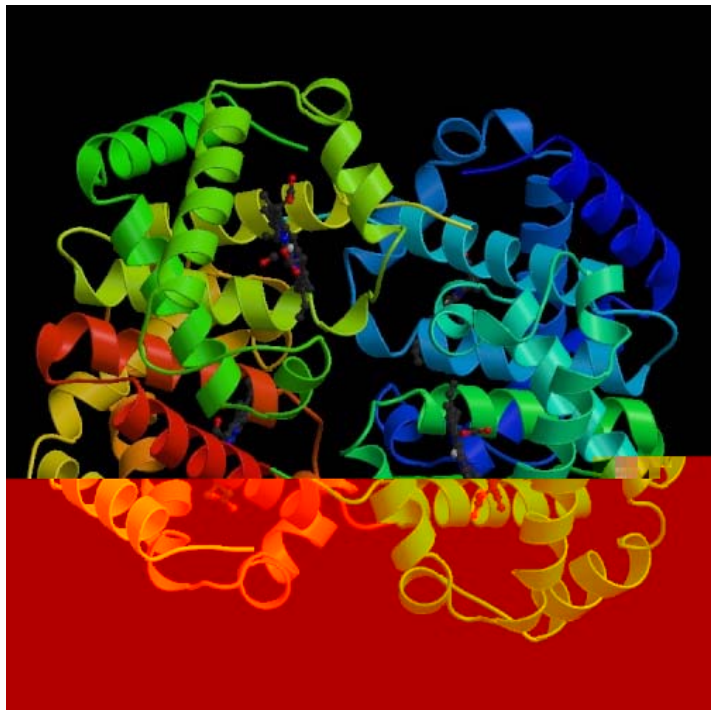




Inorganic arsenite

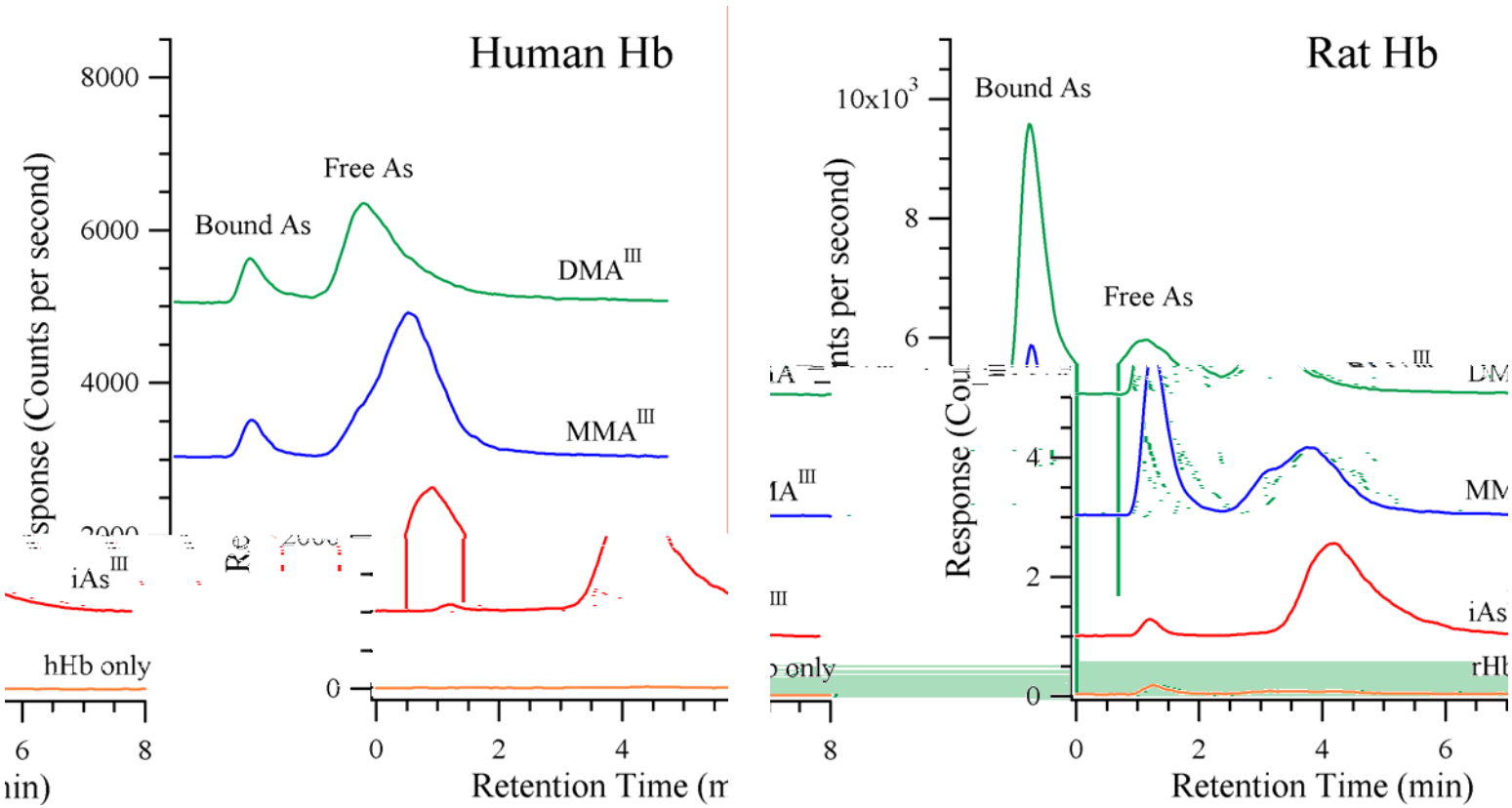
Monomethylarsonous acid

Dimethylarsinous acid



Protein

LC-ICPMS analysis of protein-bound As



4. Unidentified Arsenic Species

- **We can only study what we can measure**
- **Metabolic processes are complex and they produce various metabolites**
  - Human
  - Animal models
  - Bacteria
- **Some metabolites have not been identified and their toxicity is unknown**

Arsenic Speciation Analysis

1. Methods for arsenic speciation analysis
2. Problems of species instability
3. Binding of trivalent arsenic metabolites and arsenic in blood
4. Uncharacterized arsenic species

X. Chris Le

University of Alberta

Edmonton, Alberta, Canada